U.S. Application No.: 09/762,847

AMENDMENT G

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REMARKS

Review and reconsideration of the Office Action dated June 23, 2005 is respectfully requested.

All independent claims directed to the combustible gas have been amended to clarify that A and B are odorants that impart odor to the odorless gas. Support for the claim amendment can be found on page 1-2 the specification as originally filed.

Claim 27 has been added. Support for new Claim 27 can be found on page 2, lines 1-5, of the specification as originally filed.

No new matter has been added to the claims.

Applicants respectfully requested that the Examiner consider all arguments filed during the response to the previous Office Actions.

In addition, Applicants request that the Examiner consider the following arguments.

Issue 1 (Translation error)

Applicants note that it is the Examiner's position that the disclosure by Yoshida et al. of 2-methyl-3-isobutyl pyrazine, even if a typographical error, still provides a proper basis for maintaining his previous rejection of claims as being anticipated and/or obvious.

Basically, the mention of 2-methyl-3-isobutyl pyrazine by Yoshida on column 4, line 27-28 and column 6, line 57 is a typographical error. The word "methyl" was substituted for the

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correct word, "methoxy".

First, Applicants compared US Patent 4,487,613 (Yoshida) against the corresponding Japanese Patent 60-92396, both based on Japanese Application No. JP19840198752 in order to demonstrate that the US Patent contains a translation error.

2-methoxy-3-isobutyl pyrazine is mentioned 34 times in Yoshida, and 2-methyl-3-isobutyl pyrazine is mentioned just 2 times (column 4, line 37 and column 6, line 57). In view of the occurrence of the term "methoxyl" only twice in such a long document, the skilled person would have tried to check by comparing with the priority document and immediately noticed that there is indeed a translation error.

Please note that after intensive search, Applicants finally found out the translation of the terms methyl and methoxy.

Methyl "メチル"

Methoxy "メトキシ"

Guided by the numbers in the Japanese reference, Applicants located column 4, line 27-28 and column 6, line 57. Applicants noted that the second column of page 635 of the Japanese patent correspond to column 4 of the US patent. See attachments A-C.

Comparing the two patents, Applicant confirmed that the term "methoxy" was translated to methyl in the US patent. The

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same is true for column 6, line 57.

The Examiner indicated that on column 6, line 57, the US reference teaches a 2-methyl-3-isobutyl pyrazine. This does not make sense.

Please note that the term "2-methyl-3-isobutyl pyrazine" in column 6, line 57, is referring to Table 1, which includes the average panel results for Formulas A-G. Applicants note that Formulas A-G refer to 2-methoxy-3 isobutyl pyrazine. Nowhere in the formulas can be found the teaching of 2-methyl-3 isobutyl pyrazine; thus, the mentioning in column 6, line 57, of 2-methyl-3 isobutyl pyrazine does not make sense. Thus, this is obviously a translation error.

Furthermore, Applicants note in column 4, lines 27-28,

"Thus, when 2-methyl-3-isobutyl pyrazine is used, the amount of mixture of 2- methoxy-3 isobutyl pyrazine and 4-methyl-4-mercapto 2-pentanone"

Please note that the term "2-methyl-3-isobutyl pyrazine" is linked to 2-methoxy-3-isobutyl pyrazine. This does not make sense. Thus, this is obviously a translation error.

In both occurrences the use of the word "methyl" is a clear error because the entire patent is directed to the odor boosting qualities of 2-methoxy-3-isobutyl pyrazine.

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Finally, the mere mention of 2-methoxy-3-isobutyl pyrazine does not teach the present invention because there is no enablement for 2-methyl-3-isobutyl pyrazine in Yoshida. The use of the word 2-methyl-3-isobutyl pyrazine in Yoshida is an error, and we respectfully request that the erroneous word not be cited as prior art against the present invention.

Typographical errors arise, which can produce unintended chemical names, formulae or structures. (In re Yale, 168 USPQ 46 (1970)). These may be demonstrably patent mistakes (In re Oda, et al., 170 USPQ 268 (1970)) or latent (In re Garfinkel, 168 USPQ 662 (1971)). These occur in original articles, patents and even the Abstracting Indexes (Ex parte Henkel, et al., 130 USPQ 474 (1960)). Sometimes the "error" is deliberate as for general indexing by omitting substituent groups (Shell Development v. Watson, 113 USPQ 265 (D.DC 1957)).

Issue 2 (Rejection)

Applicants note that the present set of claims contain 8 independent claims, namely--Claims 1, 9, 19, 22, 24, 25, 26, and 27. In view that the Examiner indicated that Claims 25-26 are allowable. The following remarks are addressed to the rejected independent claims, Claim 1, 9, 19, 22, 24, and 27, because if these claims are not anticipated or obvious, it follows that none of the other rejected dependent claims are anticipated or obvious.

Regarding Claim 1

Claim 1 is directed to a method of imparting odor to an

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odorless gas by adding an odorizing composition having A, B (having specific boiling point and molecular weight), and optionally C. Furthermore A and B are odorants that act as a warning signal to warn the presence of the combustible gas.

Applicants note that the Yoshida reference fails to teach:

- 1) a nitrogen compound having a molecular weight between 80 and 160. Yoshida teaches 2-methoxy-3-isobutyl pyrazine, which has a molecular weight of 166.2224. (See Attachment B filed with Amendment E)
- 2) a nitrogen compound having a boiling point from 90 to 210°C. 2-methoxy-3-isobutyl pyrazine has a boiling point of 215°C. (See Attachment A filed with Amendment E);
- 3) a sulfur free odorizing composition.

Applicant would like to point out to the Examiner that A and B odorants that were not added to the odorless gas to increase the odor on the gas because the gas is odorless. Thus, A and B impart odor to the odorless gas.

Applicants note that the disclosed formulas of Yoshida (columns 5-6) show that preferred formulas comprise sulfide-containing components as the main ingredients. In contrast, 2-methoxy-3-isobutyl pyrazine is only present in an amount of 0.5 parts per weight. Accordingly, Yoshida mentions the use of 2-methoxy-3-isobutyl as only an "odor boosting effect" (column 6, lines 53-56). In other words, 2-methoxy-3-isobutyl pyrazine is not disclosed as a genuine odorizing agent, but rather as a

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component which can enhance the odor of the main (sulfide containing) odorizing components.

In addition, Applicants note that the claim requires that the odor must be capable of acting as a "warning signal." The odor must be unmistakable and recognizable, which is inherently found in the properties of the chemicals of components "A" and "B". (See Claim 27)

Yoshida discloses the use of 2-methoxy-3-isobutyl pyrazine as a component of a gas-odorizing agent. However, the odor of 2-methoxy-3-isobutyl pyrazine does not act as a warning signal. In fact, the odor property of 2-methoxy-3-isobutyl pyrazine is that of a green bell pepper, potato product, coffee, galbanum and green peas (see Attachment A). People know that these odors typically emanate from kitchen and food areas. Thus, these odors would not act as a warning signal for people who smell escaped gas.

Additionally, Applicants note that 2-methoxy-3-isobutyl is not the main source of odor in the compositions disclosed by Yoshida. Instead, Yoshida discloses the use of sulfides and mercaptans to create odor.

The present claim requires that the odorizing composition to be free of sulfur components.

Furthermore, the claim requires component B to have a specific range of boiling point and molecular weight. This is in view that the odorizing composition must have high volatility and evaporate leaving little residue.

Claim 9

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Claim 9 is directed to a combustible gas having: a) an odorless gas and 2) an odorizing composition having A, B (having specific boiling point and molecular weight), and optionally C.

The arguments set forth for Claim 1 apply to this claim.

Claim 19

Claim 19 is directed to a method of imparting odor to an odorless gas by adding an odorizing composition having A, B (limited by formula I and not limited by a specific boiling point and molecular weight), and optionally C.

The cited reference fails to teach that component B has 1) a structural formula I and 2) R^1-R^4 is either a hydrogen or a C_1-C_4 alkyl group.

Claim 22

Claim 22 is directed to a combustible gas having: a) an odorless gas and 2) an odorizing composition having A, B (limited by formula I and not limited by a specific boiling point and molecular weight), and optionally C.

The arguments set forth for Claim 19 apply to this claim.

Claim 24

Claim 24 is directed to an odorizing agent having: a) an odorless gas and 2) an odorizing composition having A, B (limited by formula I and not limited by a specific boiling point and molecular weight), and optionally C.

The arguments set forth for Claim 19 apply to this claim.

For the reasons set for above, Applicants respectfully

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request that the Examiner withdraw the rejection in view of the Yoshida reference.

Applicants believe that all the claims are now in conditions for allowance.

Favorable consideration and early issuance of the Notice of Allowance is respectfully requested.

Respectfully submitted,

Registration No. 45,630

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Date: October 24, 2005

CERTIFICATE OF MAILING AND AUTHORIZATION TO CHARGE

I hereby certify that the foregoing AMENDMENT G for U.S. Application No. 09/762,847 filed March 12, 2001, was deposited in first class U.S. mail, with sufficient postage, addressed to: Mail Stop: Amendments; Commissioner for Patents; P. O. Box 1450; Alexandria, VA, 22313-1450, on October 24, 2005.

The Commissioner is hereby authorized to charge any additional fees, which may be required at any time during the prosecution of this application, except for the issue fee, without specific authorization, or credit any overpayment, to Deposit Account No. 16-0877.

審によれば従来使用されている臭気附与剤の臭気の強さはその中にエタンツメルカプタンを臭気附与剤との重量に基いて約1を乃至約20を混入し、炭化水素ガス100万立方フィートにつき約0.3ポンド(0.00458/m³)の量で使用することにより増大せしめることができることが発見された。

問題を解決するための手段

(15)

作用

4 - メナル - 4 - メルカプト - 2 - ペンダノ ンを用いずペース奥気附与剤中に 2 - メトキン 化水素ガス100万立方フィート(m.c.f.)につき0.3ポンド(0.00458/m³)の扱で用いた場合、同じ炭化水米ガス100万立方フィートにつき2ポンド(0.038/m³)の使用レベルでチオフアンを単独使用した場合と同じ央気の強さを有しており、6倍の改良がなされているとになる。また、4メテル・4ーメルカプトー2ーペンタノン又にフェート・ファテルピラジンを用いると、臭気附与剤に近づく。

> Metnyl

高い臭気による衝撃。

供給ルートにおける高い安定性。

中程度の揮発性。

低い腐蝕性。

f-methyl

低い毒性。

実際、上で述べたより 10 4 - メチル - 4 - メ ルカプト - 2 - ペンタノンは食品用香料として 使用されている。

(16)

4-メチル-4-メルカプト-2-ペンタノンと 2-メトキシ-3-イソアチルピラジンと の混合物は 2-メトキシ-3-イソアチルピラジン約 1 多にして 4-メトキシ-4-メルカプト-2-ペンタノン 9 9 多乃至 2-メトキシー3-イソアチルピラジン約 5 0 多にして 4-メーチルー4-メルカプト-2-ペンタノン 5 0 多の範囲でかつペース 奥気附与剤中の混合物の質約 0.6 多乃至約 2 0 多の範囲で使用することが 好ましい。

送化水素ガス中のペース臭気附与剤の使用量では 1 0 0 万立方フィート当り約 0.0 5 ポンドから約 1 ポンド (0.0 0 0 7 5 g - 0.0 1 5 g/m²)の範囲で変化し得る。そして、好ましい範囲は 100万立方フィート当り約 0.1 万至約 0.3 ポンド (0.0 0 1 5 - 0.0 0 4 5 g/m²) である。

90.0

100.0

150.0

yl-4-mercapto-2-pentanone and/or 2-methoxy-3-isobu-f tyl pyrazine, fdeterminations were made according to the so-called "walk-in room test", the test utilized in the following tabulated examples.

According to this test, odor intensity is determined 5 by a panel of at least five persons, preferably ten or more according to the scale hereinbelow set forth.

A room with a volume of approximately 1,500 cubic feet is used. The room has facilities for ventilation between tests and is free from any significant air movement during the tests. No odor other than that of the warning agent being tested in present during the test.

A 3.2 ml ethanolic solution of the odorant is then vaporized into the room, the vaporization taking not more than 5 minutes to occur. The odorant concentration in the 3.2 ml solution is such as to give a concentration equivalent to that obtained from odorized gas (methane) diluted to 1% gas in air. Thus at a concentration corresponding to 1 pound odorant per 1 million cubic feet gas and 1 volume percent gas concentration in the room, the ethanol solution will contain 2.13 grams odorant per liter of solution.

The person vaporizing the odorant does not participate in rating the samples to be tested and at least 15 minutes is allowed between each test to allow the olfactory nerve to recover. After vaporization into the room, a five member or larger odor panel rates odor intensity of the composition according to the following scale:

Odor intensity:	Rating
No oder	0
Rarely noticeable	1
Easily noticeable	2
Strong	3

The odor intensity is judged immediately after entering the room. Any unusual character of the odor is noted and recorded. The average ratings are then calculated, rounded off to the nearest one/tenth. Finally, the 40 results are interpreted using the above scale.

Tabulated below are given average panel results determined as described above. The odor intensities of the various odorants alone or of odorant compositions containing the indicated proportions of 4-methyl-4-mercapto-2-pentanone and/or 2-methoxy-3-isobutyl pyrazine are given. The odor intensity determinations were made using four mixtures as set forth below and denoted as mixtures "A", "B", "C", "D", "E", "F" and "G":

FORMULAS	
Ingredients	Parts by Weight
Formula "A"	
Ethyl mercaptan	500.0
Dimethyl sulfide	200.0
Methyl acrylate	100.0
n-Butanai	50.0
Acetaldehyde	30.0
2-Methoxy-3-isobutyl pyrazine	که
Thiophane	100.0
Formula "B"	
Ethyl mercaptan	350.0
t-Butyl mercaptan	225.0
Dimethyl sulfide	75.0
Methyl acrylate	100.0
n-Butanal	100.0
Acetaldehyde	149.5
2-Methoxy-3-isobutyl pyrazine	0.5
Formula "C"	
Fibel mercantan	350.0

FORMULAS				
Ingredients	Parts by Weight			
t-Butyl mercaptan	225.0			
Dimethyl sulfide	75.0			
Methyl acrylate	90.0			
p-Butanal	100.0			
Acetaldehyde	150.0			
Skatole	10.0			
Formula "D"				
Ethyl mercaptan	500.0			
Ethyl mercapus	399_5			
t-Butyl mercaptan 4-methyl-4-mercapto-2-pentanone	100.0			
2-methoxy-3-isobutyl pyrazine	0.5			
Formula "E"				
	550.0			
Ethyl mercaptan	399.5			
t-Butyl mercaptan	- 50.0			
4-methyl-4-mercapto-2-pentanone	0.5			
2-methory-3-isobatyl pyrazine				
Formula "F"	590.0			
Ethyl mercaptan	399.5 .			
t-Buryl mercaptan	10.0			
4-methyl-4-mercapto-2-pentanone	0.5			
2-methoxy-3-isobutyl pyrazine				
Formula "G"	360.0			
Ethyl mercaptan	350.0			
- t-Buryl mercaptan	225.0			

	T.	ABLE I	
Example Number	Formula Code (odorant)	Concentration in Propane Gas (pounds per 10,000 gallons)	Average Rating
1	A	1.0	. 2.80
•	Ā	3.0	2.90
		1.0	2.80
	_	3.0	2.95
		1.0	1.20
			1.70
	_		2.95
			2.90
			2.80
			0.80
XT	G	1.0	0.20
	Number I II II IV V VI VII VIII IX X	Example Code Number (odorant) I A II A III B IV B V C VI C VII C VII D VIII E IX F X G	Example Code Code

Dinethyl sulfide

Methyl acrylate

Acetaldehyde

o-Botanal

35

On the basis of the testing procedure of Katz, et al (Bureau of Mines Technical Paper 480 "Intensities of Odors and Irritating Effects of Warning Agents from Flammable and Poisonous Gases" (1930)), 4-methyl-4-50 mercapto-2-pentanone and/or 2-methoxy-3-isobutyl pyrazine at a concentration equivalent to 1 pound in 1 million cubic feet of gas (methane) diluted to 1% in air gives a rating on the same basis of Table I of 2.3. The odor boosting effect of 4-methyl-4-mercapto-2-penta-55 none and/or 2-methoxy-3-isobutyl pyrazine/is clearly evident. The odor intensity of 4-methyl-4-mercapto-2pentanone and/or 2-methyl-3-isobutyl pyrazine gives rise to unexpected, unobvious and advantageous effects as when compared to ethane dimercaptan or mixtures of 60 ethane dimercaptan and thiophane, e.g. 15% ethane dimercaptan and 85% thiophane. Similar results as shown in the table are obtained with other base odorants of the prior art.

The malodorant mixture herein described is emi-65 nently suitable for use in combustible gases such as natural gas used in the home or in industry for cooking or illumination. It possesses a distinctive odor thereby providing a timely warning of escaping gas even though

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing a flow chart whereby the odorants of our invention are admixed with a hydrocarbon gas stream and the resulting fluid is 5 then distributed.

FIG. 2 is another embodiment showing the formation of the odorant mixtures of our invention and subsequent mixture with the hydrocarbon gas stream and subsequent distribution of hydrocarbon gases.

FIG. 3 is a cross section of a "Venturi" mixing apparatus section where the odorant mixture of our invention is admixed with the hydrocarbon gas stream to form an odorized gas.

FIG. 4 is an embodiment of the apparatus of FIG. 3 15 wherein the odorant gas is included in or on polymeric particles and air or nitrogen or another gas contacting the polymeric particles picks up odorant from the polymeric particles and the resulting gas mixture is admixed with a hydrocarbon gas stream.

SUMMARY OF THE INVENTION

Natural gas is usually odorized with mercaptans, alkyl sulfides, cyclic sulfides or various blends of two or more of these materials. However, when the properties 25 of these materials are compared with those of a theoretically ideal odorant, all will be found to be deficient in one or more areas. Some of the recognized features of an ideal odorant would be high odor strength, high odor impact, high stability under pipeline conditions, 30 moderate volatility, low corrosivity and low toxicity. Of the above features, odor strength (basically odor detectability of the material at low concentrations) and odor impact (the ability of a particular odor to arrest attention) are probably of primary importance because 35 these are the features which allow the detection of gas before it reaches hazardous concentrations. It is generally recognized that of the above materials, the mercaptans offer the highest odor intensity and the highest odor impact. However, it is also known that under 40 about 3%. certain pipeline conditions mercaptans are not stable because they are readily oxidized to essentially nonodorous materials. The alkyl sulfides and cyclic sulfides offer greater stability than mercaptans and have odor intensities similar to mercaptans, but generally have 45 been less widely accepted because they lack the odor impact offered by mercaptans.

Furthermore, U.S. Pat. No. 3,545,949 teaches that of the mercaptans, t-butyl mercaptan has been preferred to be used commercially as a gas odorant because it is the 50 least susceptible of the lower alkyl mercaptans to oxidation and consequently is the base for the majority of the gas odorants used today. U.S. Pat. No. 3,545,949 further teaches that n-hexyl mercaptan and cyclohexyl mercaptan overcome a number of problems theretofore existing in the field of odorization of natural gas.

Furthermore, in U.S. Pat. No. 3,404,971 it was found that odor intensity of conventional malodorants can be increased by incorporation in them of a small amount of ethane dimercaptan ranging from about 1% up to about 60 20% by weight based on ethane dimercaptan and malodorant and used in a dosage of about 0.3 pounds per million cubic feet of hydrocarbon gas.

It has now been found that the odor intensity of all of the foregoing conventional and prior art malodorants 65 can be increased by incorporation in them of a small amount of 4-methyl-4-mercapto-2-pentanone and/or 2-methoxy-3-isobutyl pyrazine, the amount of 4-methyl-

4-mercapic-2-pentanone in the odorant can range from about 10% up to about 30%; preferably about 20% by weight based on total malodorant. For example, a mixture of 20% 4-methyl-4-mercapto-2-pentanone and 80% thiophane used in a dosage of 0.3 pounds per million cubic feet (m.c.f.) of hydrocarbon gas has the same odor intensity as thiophane alone used at a dosage level of 2 pounds per million cubic feet of the same hydrocarbon gas indicating a six-fold improvement. In addition,

when using 4-methyl-4-mercapto-2-pentanone or 2-7 methoxy-3-isobutyl pyrazine, the odorant approaches ideality:

high odor strength;
high odor impact;
high stability under pipeline conditions;
moderate volatility;
low corrosivity; and
low toxicity.

Indeed, 4-methyl-4-mercapto-2-pentanone is used as a 20 food flavorant as set forth supra.

When using a mixture of 4-methyl-4-mercapto-2-pentanone and 2-methoxy-3-isobutyl pyrazine, the amount of mixture of 4-methyl-4-mercapto-2-pentanone and 2-methoxy-3-isobutyl pyrazine may range from about 1 up to about 25% depending upon the proportion of 2-methoxy-3-isobutyl pyrazine; in the 4-methyl-4-mercapto-2-pentanone. Thus, when 95% 2-methyl-3-isobutyl pyrazine is used, the amount of mixture of 2-methoxy-3-isobutyl pyrazine and 4-methyl-4-mercapto-2-pentanone in the odorant can be as low as 1% and even lower (0.5%). When using a mixture containing 50% 4-methyl-4-mercapto-2-pentanone and 50% 2-methoxy-3-isobutyl pyrazine/ the range may be from about 2% up to about 25% with a preferred range of from about 2 up to about 5% in the base odorant.

When using only 2-methoxy-3-isobutyl pyrazine in the base odorant without the 4-methyl-4-mercapto-2-pentanone, the range of 2-methoxy-3-isobutyl pyrazine in the base odorant may vary from about 0.4% up to about 3%.

It is preferred to use mixtures of 4-methyl-4-mercap-to-2-pentanone and 2-methoxy-3-isobutyl pyrazine/ranging from about 1% 2-methoxy-3-isobutyl pyrazine/and 99% 4-methoxy-4-mercapto-2-pentanone up to about 50% 2-methoxy-3-isobutyl pyrazine and 50% 4-methyl-4-mercapto-2-pentanone with a range of mixture in the base odorant of from about 0.6% up to about 20%.

The dosage of base odorant in the hydrocarbon gas may vary from about 0.05 pounds per million cubic feet up to about 1 pound per million cubic feet with a preferred range of from about 0.1 up to about 0.3 pounds per million cubic feet.

The method of mixing the conventional or base odorant and the odorant boosting B 4-methyl-4-mercapto-2-pentanone and/or 2-methoxy-3-isobutyl pyrazine is not critical. Since these materials are relatively low boiling liquids, one or the other can be added to the other in the indicated proportion ranges in a manner applicable to the mixing of any compatible liquids. However, it is advisable to utilize mixing apparatus as set forth in the detailed description of the drawings, infra, or apparatus as disclosed in U.S. Pat. No. 3,907,515 issued on Sept. 23, 1975 or U.S. Pat. No. 4,025,315 issued on May 24, 1977, the disclosures of which are incorporated by reference herein.

To show the odor boosting effectiveness of the odorant mixture of the present invention containing 4-meth-

) reference back.

104 S *

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